Supporting Information for

Substituent Effects on Energetics of Peptide-Carboxylate Hydrogen Bonds as Studied by ^{1}H NMR Spectroscopy: Implications for Enzyme Catalysis

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Crystal Data and Structure Analysis Details for 2-(4-nitrobenzamido)benzoic acid (1)

Empirical formula	$C_{14}\ H_{10}N_2O_5$
Formula weight	286.24
Crystallization solvent	THF/Hexanes
Crystal shape	plate
Crystal color	colorless
Crystal size	0.17 x 0.26 x 0.34 mm
Data Collection	
Preliminary photograph(s)	rotation
Type of diffractometer	Bruker SMART 1000 ccd
Wavelength	0.71073 Å MoK

Data collection temperature	100 K
Theta range for 9931 reflections used	
in lattice determination	2.20 to 39.03°
Unit cell dimensions	a = 27.6966(11) Å a= 90°
b = 4.8683(2) Å	b= 118.152(2)°
c = 21.0108(9) Å	g = 90°
Volume	2497.85(18) $Å^3$
Z	8
Crystal system	monoclinic
Space group	C 1 2/c 1 (# 15)
Density (calculated)	1.522 g/cm^3
F(000)	1184
Theta range for data collection	1.7 to 41.1°
Completeness to theta = 25.000°	100.0%
Index ranges	-50 £ h £ 50, -8 £ k £ 8, -38 £ l £ 38
Data collection scan type	scans
Reflections collected	60562
Independent reflections	8041 [R_{int}= 0.0477]
Reflections > 2s(I)	5863
Average s(I)/(net I)	0.0364
Absorption coefficient	0.12 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.9295
Structure Solution and Refinement	
Primary solution method	dual
Secondary solution method	difmap
Hydrogen placement	geom
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8041 / 0 / 230
Treatment of hydrogen atoms	refall

Goodness-of-fit on F^2	3.51
Final R indices [I>2s(I), 5863 reflections]	R1 = 0.0708, wR2 = 0.0909
R indices (all data)	R1 = 0.0989, wR2 = 0.0923
Type of weighting scheme used	calc
Weighting scheme used	
Max shift/error	0.001
Average shift/error	0.000
Extinction coefficient	0
Largest diff. peak and hole	1.24 and -0.74 e·Å^{-3}

DIAMOND 3 (Crystal Impact, 1999)

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for bue001. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

x	y	z	U_{eq}	
O(1)	5130(1)	7228(2)	4581(1)	49(1)
O(2)	5044(1)	10012(2)	3744(1)	37(1)
O(3)	2430(1)	13184(1)	3061(1)	18(1)
O(4)	2507(1)	5019(1)	4489(1)	13(1)
O(5)	1813(1)	3917(1)	4704(1)	15(1)
N(1)	4860(1)	8815(2)	4093(1)	21(1)
N(2)	2353(1)	9137(2)	3565(1)	12(1)
C(1)	3517(1)	8300(2)	4097(1)	16(1)
C(2)	4060(1)	7808(2)	4271(1)	18(1)
C(3)	4288(1)	9338(2)	3922(1)	15(1)
C(4)	3999(1)	11350(2)	3418(1)	16(1)

C(5)	3461(1)	11831(2)	3258(1)	15(1)
C(6)	3214(1)	10303(2)	3587(1)	11(1)
C(7)	2627(1)	11021(2)	3373(1)	11(1)
C(8)	1820(1)	9328(2)	3486(1)	11(1)
C(9)	1441(1)	11256(2)	3021(1)	13(1)
C(10)	917(1)	11385(2)	2952(1)	15(1)
C(11)	755(1)	9610(2)	3335(1)	17(1)
C(12)	1125(1)	7682(2)	3792(1)	14(1)
C(13)	1658(1)	7507(2)	3877(1)	11(1)
C(14)	2030(1)	5393(2)	4377(1)	11(1)

Table 3. Bond lengths [Å] and angles [°] for 1.

O(1)-N(1)	1.2177(12)
O(2)-N(1)	1.2200(11)
O(3)-C(7)	1.2242(10)
O(4)-C(14)	1.2415(10)
O(5)-C(14)	1.3189(10)
O(5)-H(5)	0.883(14)
N(1)-C(3)	1.4730(12)
N(2)-C(7)	1.3674(11)
N(2)-C(8)	1.4064(11)
N(2)-H(2)	0.830(12)
C(1)-H(1)	0.960(11)
C(1)-C(2)	1.3922(13)
C(1)-C(6)	1.3978(12)
C(2)-H(2A)	0.920(12)
C(2)-C(3)	1.3868(13)
C(3)-C(4)	1.3863(13)

C(4)-H(4)	0.956(11)
C(4)-C(5)	1.3845(13)
C(5)-H(5A)	0.944(11)
C(5)-C(6)	1.3950(12)
C(6)-C(7)	1.5094(12)
C(8)-C(9)	1.4036(12)
C(8)-C(13)	1.4195(12)
C(9)-H(9)	0.940(10)
C(9)-C(10)	1.3919(13)
C(10)-H(10)	0.975(11)
C(10)-C(11)	1.3900(13)
C(11)-H(11)	0.950(11)
C(11)-C(12)	1.3876(13)
C(12)-H(12)	0.945(11)
C(12)-C(13)	1.4014(12)
C(13)-C(14)	1.4843(12)
C(14)-O(5)-H(5)	108.2(9)
O(1)-N(1)-O(2)	122.96(9)
O(1)-N(1)-C(3)	118.54(8)
O(2)-N(1)-C(3)	118.50(8)
C(7)-N(2)-C(8)	128.17(7)
C(7)-N(2)-H(2)	117.6(8)
C(8)-N(2)-H(2)	114.2(8)
C(2)-C(1)-H(1)	118.8(7)
C(2)-C(1)-C(6)	120.32(8)
C(6)-C(1)-H(1)	120.9(7)
C(1)-C(2)-H(2A)	120.6(7)
C(3)-C(2)-C(1)	118.23(9)
C(3)-C(2)-H(2A)	121.1(7)
C(2)-C(3)-N(1)	118.86(8)
C(4)-C(3)-N(1)	118.33(8)

C(4)-C(3)-C(2)	122.81(8)
C(3)-C(4)-H(4)	120.4(6)
C(5)-C(4)-C(3)	118.09(8)
C(5)-C(4)-H(4)	121.5(6)
C(4)-C(5)-H(5A)	120.2(7)
C(4)-C(5)-C(6)	120.90(8)
C(6)-C(5)-H(5A)	118.8(7)
C(1)-C(6)-C(7)	124.25(8)
C(5)-C(6)-C(1)	119.63(8)
C(5)-C(6)-C(7)	116.11(7)
O(3)-C(7)-N(2)	124.42(8)
O(3)-C(7)-C(6)	120.29(8)
N(2)-C(7)-C(6)	115.27(7)
N(2)-C(8)-C(13)	119.46(7)
C(9)-C(8)-N(2)	121.66(8)
C(9)-C(8)-C(13)	118.87(8)
C(8)-C(9)-H(9)	120.3(6)
C(10)-C(9)-C(8)	120.27(8)
C(10)-C(9)-H(9)	119.5(6)
C(9)-C(10)-H(10)	118.4(6)
C(11)-C(10)-C(9)	121.12(8)
C(11)-C(10)-H(10)	120.4(6)
C(10)-C(11)-H(11)	121.2(6)
C(12)-C(11)-C(10)	119.12(8)
C(12)-C(11)-H(11)	119.7(6)
C(11)-C(12)-H(12)	120.6(6)
C(11)-C(12)-C(13)	121.24(9)
C(13)-C(12)-H(12)	118.1(6)
C(8)-C(13)-C(14)	122.62(7)
C(12)-C(13)-C(8)	119.38(8)
C(12)-C(13)-C(14)	118.00(8)

O(4)-C(14)-O(5)	121.79(8)
O(4)-C(14)-C(13)	123.88(8)
O(5)-C(14)-C(13)	114.32(7)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for bue001. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	235(4)	599(6)	666(7)	397(5)	245(4)	208(4)
O(2)	198(4)	518(5)	461(5)	190(4)	202(4)	31(4)
O(3)	189(3)	129(3)	226(4)	67(3)	113(3)	39(2)
O(4)	123(3)	114(3)	146(3)	25(2)	61(2)	16(2)
O(5)	148(3)	136(3)	173(3)	46(2)	89(3)	18(2)
N(1)	142(4)	240(4)	262(4)	18(4)	99(3)	5(3)
N(2)	113(3)	88(3)	149(4)	36(3)	61(3)	26(3)
C(1)	159(4)	150(4)	198(5)	55(3)	108(4)	16(3)
C(2)	154(4)	178(5)	219(5)	75(4)	88(4)	47(3)
C(3)	108(4)	177(4)	169(4)	-12(3)	65(3)	-6(3)
C(4)	154(4)	176(4)	158(4)	17(3)	83(4)	-28(3)
C(5)	154(4)	145(4)	129(4)	21(3)	59(4)	-3(3)
C(6)	132(4)	101(4)	110(4)	-9(3)	60(3)	-2(3)
C(7)	136(4)	110(4)	97(4)	-10(3)	59(3)	-7(3)
C(8)	111(4)	95(4)	108(4)	-27(3)	45(3)	-3(3)

C(9)	153(4)	104(4)	119(4)	4(3)	50(3)	10(3)
C(10)	136(4)	130(4)	151(4)	2(3)	29(3)	37(3)
C(11)	122(4)	170(4)	208(5)	-5(4)	69(4)	15(3)
C(12)	133(4)	135(4)	165(5)	1(3)	70(4)	-6(3)
C(13)	110(4)	91(4)	108(4)	-13(3)	40(3)	3(3)
C(14)	140(4)	86(4)	97(4)	-22(3)	53(3)	-12(3)

Table 5. Hydrogen coordinates (x 10^3) and isotropic displacement parameters ($Å^2$x 10^3) for bue001.

x	y	z	U_{iso}	
H(1)	336(1)	730(2)	435(1)	18(3)
H(2A)	426(1)	652(2)	461(1)	26(3)
H(4)	417(1)	1235(2)	318(1)	18(3)
H(5A)	325(1)	1316(2)	291(1)	19(3)
H(9)	154(1)	1244(2)	274(1)	12(3)
H(10)	66(1)	1278(2)	264(1)	19(3)
H(11)	40(1)	973(2)	330(1)	18(3)
H(12)	102(1)	645(2)	406(1)	14(3)
H(2)	252(1)	771(2)	377(1)	21(3)
H(5)	206(1)	274(3)	499(1)	41(4)

Table 6. Hydrogen bonds for bue001 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...O(3)#1	0.830(12)	2.606(12)	3.1269(10)	122.1(10)
N(2)-H(2)...O(4)	0.830(12)	2.015(12)	2.6820(10)	136.9(10)
O(5)-H(5)...O(4)#2	0.883(14)	1.785(14)	2.6610(9)	171.6(13)

Cartesian coordinates for the optimized structures at the B3LYP/6-31+G(d) levels

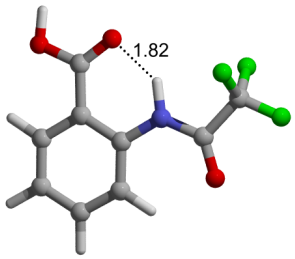


Table Cartesian coordinates for 12a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.955889	0.322786	-0.000106
2	6	0	3.270639	-0.177464	-0.000100
3	6	0	3.522151	-1.543892	-0.000030
4	6	0	2.443929	-2.433794	0.000046
5	6	0	1.129530	-1.972600	0.000048
6	6	0	0.863594	-0.592576	-0.000025
7	1	0	4.092768	0.528562	-0.000156
8	1	0	4.544040	-1.910999	-0.000031
9	1	0	2.622257	-3.505858	0.000104

10	1	0	0.302492	-2.668385	0.000105
11	6	0	1.739072	1.784962	-0.000183
12	8	0	0.647883	2.348071	0.000108
13	8	0	2.882053	2.507694	0.000080
14	1	0	2.618894	3.446983	0.000253
15	7	0	-0.448243	-0.088939	-0.000029
16	1	0	-0.495091	0.934341	-0.000112
17	6	0	-1.618314	-0.788639	0.000038
18	8	0	-1.772446	-1.996390	0.000083
19	6	0	-2.858837	0.155373	-0.000002
20	9	0	-2.852993	0.960981	-1.091566
21	9	0	-2.853172	0.960812	1.091687
22	9	0	-3.993114	-0.544239	-0.000148

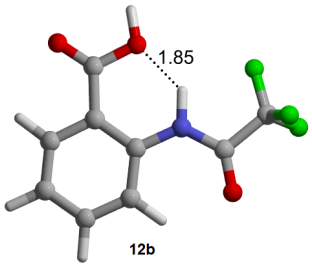


Table Cartesian coordinates for 12b

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000008237	-0.000010490	0.000017788
2	6	-0.000007985	0.000015559	-0.000012200
3	6	-0.000001493	-0.000010995	-0.000012922
4	6	0.000007030	-0.000005063	0.000014037
5	6	-0.000011704	0.000008262	-0.000017917
6	6	0.000022360	-0.000017957	0.000018279

7	1	-0.000004299	-0.000003643	0.000002874
8	1	-0.000003364	-0.000002925	-0.000001525
9	1	0.000002135	-0.000001336	-0.000004705
10	1	0.000004108	0.000001082	-0.000000595
11	6	-0.000006752	0.000036127	-0.000038960
12	8	-0.000003113	-0.000018093	0.000013480
13	7	-0.000016654	-0.000005252	-0.000034345
14	1	-0.000005143	0.000017949	0.000006219
15	6	0.000003236	0.000028868	0.000019491
16	8	0.000005488	-0.000004325	-0.000009266
17	8	-0.000006504	-0.000034392	0.000029637
18	1	-0.000004726	0.000001249	0.000003733
19	6	0.000022801	0.000000260	0.000015720
20	9	-0.000011002	0.000006631	-0.000010603
21	9	0.000003671	-0.000014089	-0.000002115
22	9	0.000003673	0.000012572	0.000003894

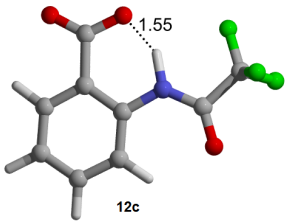
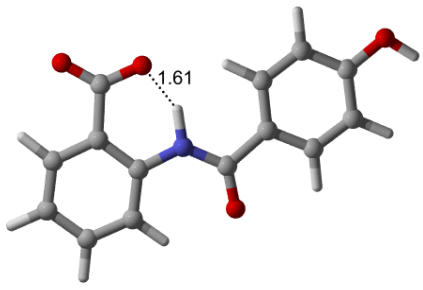


Table Cartesian coordinates for 12c

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.978434	0.406338	-0.001532
2	6	0	-3.298755	-0.055376	0.008041

3	6	0	-3.603441	-1.417870	0.009081
4	6	0	-2.564295	-2.352789	0.000643
5	6	0	-1.233901	-1.931649	-0.008489
6	6	0	-0.935381	-0.556548	-0.009820
7	1	0	-4.077697	0.701139	0.014966
8	1	0	-4.640862	-1.747339	0.016455
9	1	0	-2.782960	-3.419215	0.001290
10	1	0	-0.423135	-2.648239	-0.014561
11	6	0	-1.738466	1.936083	-0.002103
12	8	0	-0.515112	2.313067	-0.016111
13	7	0	0.386076	-0.057539	-0.019452
14	1	0	0.340095	1.017465	-0.024010
15	6	0	1.527275	-0.758679	-0.013414
16	8	0	1.699721	-1.979601	-0.004899
17	8	0	-2.749141	2.663140	0.010665
18	6	0	2.809584	0.118930	0.001597
19	9	0	3.486131	-0.060739	1.166168
20	9	0	2.589526	1.443556	-0.130447
21	9	0	3.645807	-0.249986	-1.000080

Table Cartesian coordinates for compound 7



Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	-2.764003	0.616700	0.000201
2	6	0	-4.149260	0.420997	-0.000455
3	6	0	-4.717795	-0.854618	-0.000700
4	6	0	-3.881327	-1.974798	-0.000298
5	6	0	-2.494309	-1.823941	0.000360
6	6	0	-1.926595	-0.534818	0.000605
7	1	0	-4.765351	1.315266	-0.000794
8	1	0	-5.799978	-0.972989	-0.001194
9	1	0	-4.305252	-2.977933	-0.000500
10	1	0	-1.836525	-2.683083	0.000585
11	6	0	-2.240444	2.076329	0.000436
12	8	0	-0.968024	2.230039	0.001482
13	8	0	-3.098671	2.979621	-0.000391
14	7	0	-0.541025	-0.305777	0.001452
15	1	0	-0.384350	0.733016	0.001932
16	6	0	0.486838	-1.189919	-0.000129
17	8	0	0.365107	-2.426133	-0.001416
18	6	0	1.868312	-0.572907	-0.000008
19	6	0	2.130384	0.810067	-0.001204
20	6	0	2.957245	-1.455578	0.001024
21	6	0	3.440571	1.288592	-0.001346
22	1	0	1.322406	1.536849	-0.002088
23	6	0	4.269980	-0.985827	0.000990
24	1	0	2.749030	-2.520906	0.001738
25	6	0	4.511473	0.391677	-0.000209
26	1	0	3.640374	2.356270	-0.002311
27	1	0	5.103902	-1.688243	0.001822
28	8	0	5.787777	0.914589	-0.000353
29	1	0	6.426989	0.185510	0.000482

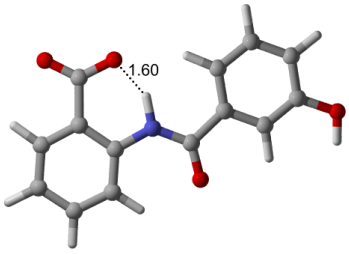


Table Cartesian coordinates for compound 9

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.807895	0.444940	0.000065
2	6	0	4.157751	0.077481	-0.000037
3	6	0	4.561378	-1.259435	-0.000033
4	6	0	3.591242	-2.266004	0.000069
5	6	0	2.234037	-1.942487	0.000166
6	6	0	1.833047	-0.592337	0.000148
7	1	0	4.881103	0.887370	-0.000094
8	1	0	5.620092	-1.512791	-0.000130
9	1	0	3.886285	-3.314258	0.000112
10	1	0	1.474377	-2.712884	0.000186
11	6	0	2.470531	1.958621	0.000042
12	8	0	3.434700	2.747484	0.000090
13	8	0	1.227098	2.268528	0.000001
14	7	0	0.486522	-0.191241	0.000283
15	1	0	0.460993	0.860543	0.000268
16	6	0	-0.640902	-0.940656	-0.000194
17	8	0	-0.677007	-2.182383	-0.000587
18	6	0	-1.939005	-0.154350	-0.000132
19	6	0	-2.023227	1.247642	-0.000235

20	6	0	-3.118913	-0.911755	0.000060
21	6	0	-3.279975	1.860594	-0.000190
22	1	0	-1.134216	1.870967	-0.000325
23	6	0	-4.363824	-0.286307	0.000126
24	1	0	-3.026593	-1.995882	0.000108
25	6	0	-4.456013	1.107929	-0.000039
26	1	0	-3.340656	2.946359	-0.000286
27	1	0	-5.434642	1.580028	-0.000015
28	8	0	-5.543388	-1.006380	0.000360
29	1	0	-5.327749	-1.952027	0.000395

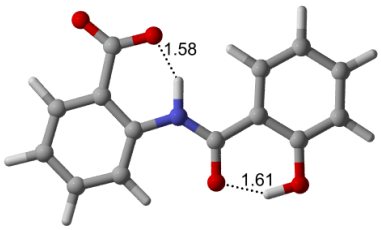


Table Cartesian coordinates for compound 10

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.660358	0.493108	-0.000057
2	6	0	-4.008571	0.120091	-0.000074
3	6	0	-4.405515	-1.218523	-0.000013
4	6	0	-3.430861	-2.220281	0.000066
5	6	0	-2.075065	-1.890543	0.000088
6	6	0	-1.680801	-0.538987	0.000032
7	1	0	-4.735446	0.926741	-0.000144
8	1	0	-5.462844	-1.477046	-0.000029

9	1	0	-3.720557	-3.269833	0.000113
10	1	0	-1.314833	-2.659520	0.000152
11	6	0	-2.329913	2.007753	-0.000152
12	8	0	-1.086439	2.321071	-0.000144
13	8	0	-3.295560	2.793021	-0.000203
14	7	0	-0.335935	-0.122391	0.000062
15	1	0	-0.329538	0.935056	0.000036
16	6	0	0.796787	-0.848060	0.000121
17	8	0	0.813392	-2.110588	0.000099
18	6	0	2.092211	-0.092995	0.000064
19	6	0	2.162677	1.314815	0.000015
20	6	0	3.311275	-0.826512	0.000060
21	6	0	3.385474	1.980521	-0.000029
22	1	0	1.253416	1.908907	0.000017
23	6	0	4.541233	-0.146360	0.000016
24	6	0	4.577422	1.243099	-0.000028
25	1	0	3.405822	3.066920	-0.000062
26	1	0	5.451008	-0.740623	0.000016
27	8	0	3.346918	-2.176739	0.000093
28	1	0	2.384504	-2.466387	0.000112
29	1	0	5.537569	1.755644	-0.000062
